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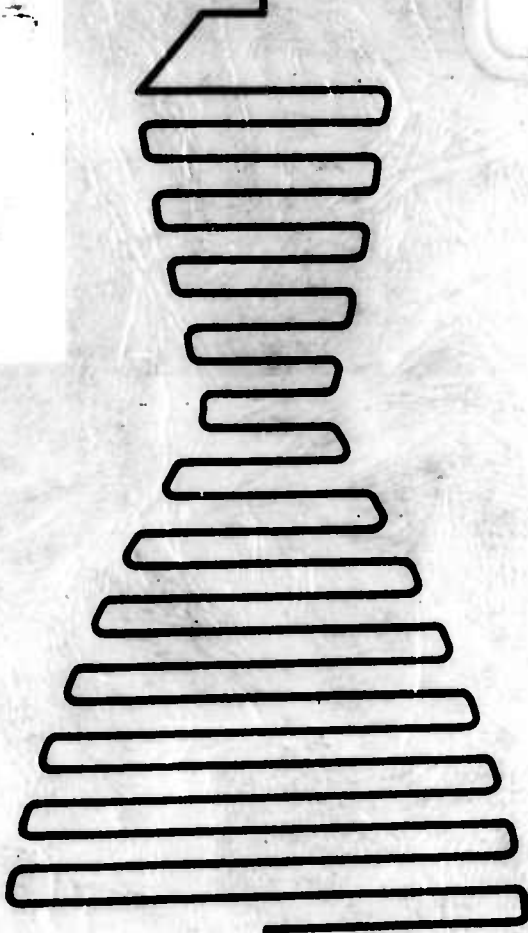
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RESEARCH ON FLUORINE PROPELLANTS  
QUARTERLY PROGRESS REPORT FOR  
PERIOD ENDING 15 JUNE 1960

**ROCKETDYNE**

A DIVISION OF NORTH AMERICAN AVIATION, INC.  
6633 CANOGA AVENUE  
CANOGA PARK, CALIFORNIA

Contract Nonr 1818(00)

GO 9243

**PREPARED BY**

Experimental Chemistry Group

**APPROVED BY**

*R. J. Thompson, Jr.*  
R. J. Thompson, Jr.  
Director  
Research

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### **FOREWORD**

This report was prepared by the Experimental Chemistry Group of the Research Department of Rocketdyne. Support for this research effort was obtained from the Office of Naval Research under Contract Nonr-1818(00). Supplementary funds were provided by the Advanced Projects Research Agency under ARPA Order No. 23-60, Amend. 6. This report covers the period 16 March 1960 through 15 June 1960.

The responsible scientist for this work is Dr. Emil A. Lawton. Dr. Walter Maya, John Q. Weber, David F. Sheehan and Michael Warner were full time associates on this project and Richard Wilson half time. The analytical support and infrared interpretations were furnished by E. F. C. Cain.

### **ABSTRACT**

The solid oxidizer reported previously has been identified as unsymmetrical difluorourea,  $F_2NCONH_2$ , mp 41.0 to 41.5 C. The evidence for the structure of the compound and some of its properties are described. The results of more fluorinations are described and additional reactions of difluoramine are reported. The heat of dissociation of the  $RbF \cdot HNF_2$  complex has been determined and evidence is presented that CsF forms more than one complex.

Difluorodiazine and dioxygen difluoride,  $O_2F_2$ , were found not to react with one another but it was observed that electrical excitation of nitrogen-fluorine gas mixtures at 196 C yielded  $NF_3$  and an unstable species which has not yet been identified.

(CONFIDENTIAL ABSTRACT)

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**INTRODUCTION**

The synthesis of high-performance oxidizers is an ultimate goal of the research in this program. The approach utilized has been the study of the chemistry of compounds containing NF and OF bonds since large gains in impulse over that achieved with conventional oxidizers could be obtained with oxidizers containing these groups.

In the previous report (Ref. 1), we reported the isolation of crude solid products from the urea fluoridate residues containing up to 22 percent active fluorine. We have isolated the principal constituent as a pure compound and identified it as difluorourea. In addition, the acid properties of difluoramine were studied further through its reactions with mild bases, such as the alkali metal fluorides. Additional fluorinations are reported as well as some of the results obtained with dioxygen difluoride,  $O_2F_2$ . Reactions initiated by electrical discharge are also discussed.

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DISCUSSION

DIFLUOROUREA

The separation of crude solid products from the residues obtained on the distillation of fluorinated urea liquids has already been reported (Ref. 1, 2). The most interesting facet was the isolation of small quantities of fine needles melting from 40.7 to 41.1 C. The solid was found to react slowly with glass and mercury, and to be rather hygroscopic. Larger quantities were obtained by extraction of the solid residues with dichloromethane, evaporation of the solvents at low temperatures and low pressures in polyethylene apparatus and then subliming the crude residue at somewhat reduced pressures. The highest melting range observed for the solid was 41.0-41.5 C. From elemental analyses and infrared spectra, the compound has been identified as uns-difluorourea,  $\text{NF}_2\text{CONH}_2$ .

The infrared spectra of difluorourea were obtained both as a solution in dichloromethane (Fig. 1) and as a mineral oil mull (Fig. 2). The details of the spectra are described in Table 1.

Both spectra were obtained on a Beckman IR-7 spectrophotometer; the solution spectrum was run with a solvent reference. The evidence is as follows:

1. NH Stretching Modes

Medium intensity absorptions in dilute solution at 3520 and 3420  $\text{cm}^{-1}$  correspond to the free NH stretch frequency of a primary amide,  $-\text{N}\begin{smallmatrix} \text{H} \\ \diagup \\ \text{H} \end{smallmatrix}$ .

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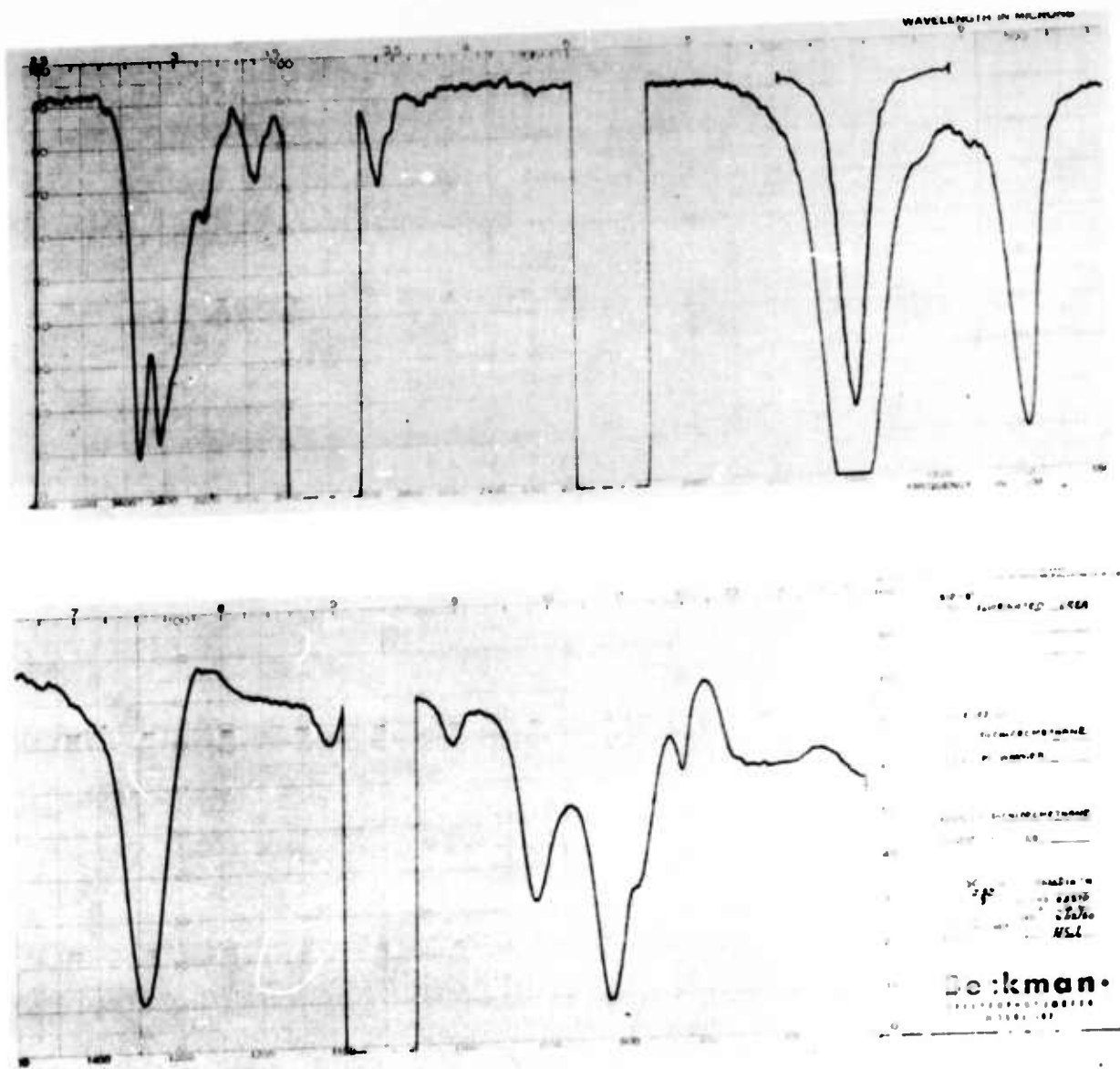


Figure 1. Infrared Spectrum of Difluorourea in Solution

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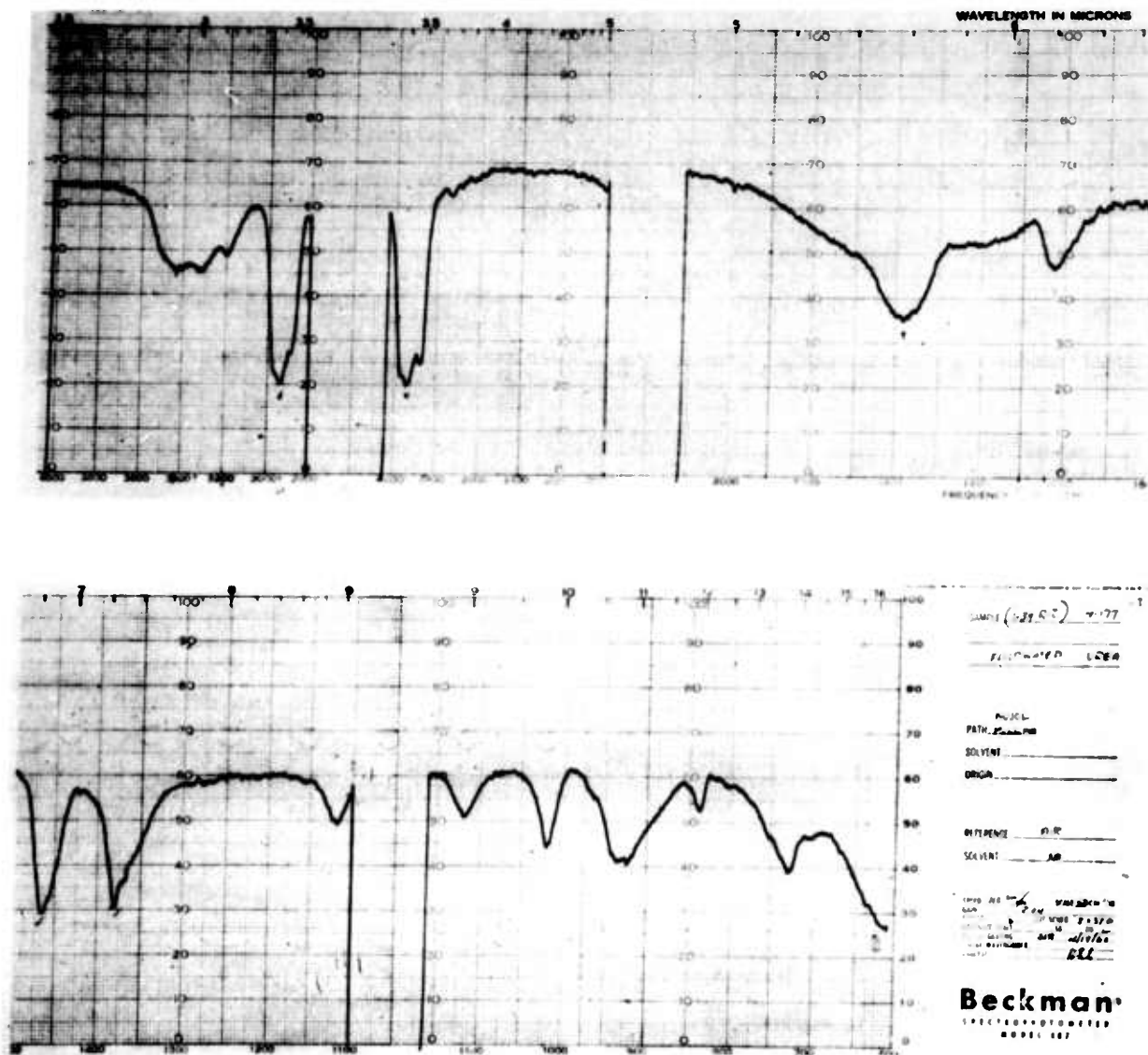


Figure 2. Infrared Spectrum of Difluorourea in a Mineral Oil Mull

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**TABLE 1**

**INFRARED SPECTRUM OF UNSYMMETRICAL DIFLUOROURREA**

Dilute Sol'n	Solid State	Intensity	Assignment
$\text{cm}^{-1}$	$\text{cm}^{-1}$ (Nujol Mull)		
3520		m	N-H stretch (free)
	3425	m	N-H stretch (bonded)
3420		m	N-H stretch (free)
	3320	m	N-H stretch (bonded)
3200	3200	v	—
2940	—	v	—
1803	1790	s	Amide I
1592	1613	m	Amide II
1345	1343	m	—
1115	1118	v	—
1018	1020	m	—
925	925	m	N-F (tentative)
892	—	v	—
836	836	v	—

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In the solid state these absorptions are shifted to lower frequencies, 3425 and 3320  $\text{cm}^{-1}$  respectively, which would be expected due to the association of a primary amide.

2. CO Absorption (Amide I) Band

In dilute solution, a strong band at 1803  $\text{cm}^{-1}$  corresponding to a carbonyl absorption with a strong electronegative group in the C position. (The carbonyl stretch of  $\text{CH}_3\text{C}^{\text{O}}\text{NF}_2$  has been reported at ca. 1803  $\text{cm}^{-1}$ .) (Ref. 3) In the solid state, this absorption shifts to a lower frequency, 1790  $\text{cm}^{-1}$ . The direction of the shift is as expected.

3.  $\text{NH}_2$  Deformation (Amide II) Band

In dilute solution, a strong band at 1592  $\text{cm}^{-1}$  corresponding to the Amide II absorption of a primary amide. In the solid state, this absorption is shifted to a higher frequency, 1613  $\text{cm}^{-1}$ . The direction of the shift is as expected.

4. The absorptions at 1803  $\text{cm}^{-1}$  and 1592  $\text{cm}^{-1}$  in the dilute solution of the material are shifted in the spectrum of the solid. These shifts confirm the assignment of the Amide I and Amide II Bands of a primary amide to these absorptions. (Ref. 4)

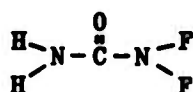
5.  $\text{NF}_2$  Grouping

The large frequency shift of the Amide I Band from a nominal 1690  $\text{cm}^{-1}$  in dilute solution to 1803  $\text{cm}^{-1}$  indicates the presence of a strong electronegative group attached to the carbonyl carbon atom. A strong absorption at 925  $\text{cm}^{-1}$  has been assigned to the N-F stretch frequency and is compatible with the remainder of the spectrum.

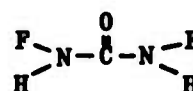
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6. On the basis of the infrared spectrum, the solid material may be represented by Structure I. Structure II is not compatible with the infrared spectrum.



**I**  
Primary Amide



**II**  
Secondary Amide

The infrared structure was confirmed by wet chemical techniques. Analyses were carried out to determine active fluorine and total fluorine. By modification of the Kjeldahl nitrogen technique it was possible to differentiate between the N-H<sub>2</sub> structure and the N-F<sub>2</sub> structure. The results of these analyses are shown in Table 2.

**TABLE 2**

**SUMMARY OF WET CHEMICAL ANALYSES**

Sought	Calc.	Found
Active Fluorine	39.6	38.
Total Fluorine	39.6	38.6
Total Nitrogen	29.2	29.3
Amino Nitrogen (NH <sub>2</sub> )	14.6	14.6



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The mass spectrum of a sample of moderate purity gave principally peaks for  $\text{HNF}_2$ ,  $\text{HNCO}$  and some difluorodiazine. The compound is very soluble in water, and soluble in dichloromethane and tetrahydrofuran. Caution in handling is required since it is a vesicant and lachrymator. Difluoro-urea is stable to at least 50 C but it can be detonated by heat.

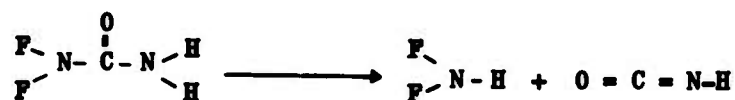
### FLUORINATION OF NITROGEN COMPOUNDS

Work has continued on the fluorination of urea with two objectives in mind: first, to supply difluoramine and difluorourea for other chemical syntheses, and second, to obtain a better understanding of the fluorination itself. In view of the relatively drastic conditions of direct fluorination it is not surprising that the percent of both active fluorine and total fluorine content vary considerably from one fluorination to another. Examination of the data compiled from all previous fluorinations and distillations indicated that mechanical difficulties such as plugging, channeling of the fluorine-nitrogen mixture through the solid, and caking up of the partially fluorinated product, caused some of the variability observed. These difficulties might cause incomplete fluorination or bring about local hot spots which alter the products obtained even though equivalent or slightly excess amounts of fluorine are used in all fluorinations.

The variability in the amount of difluoramine obtained by vacuum distillation, even from quite similar liquids, tends to suggest that either these samples are in different stages of fluorination, or that there is an intermediate compound which subsequently decomposes to different degrees depending on the conditions of the reaction and subsequent handling of the liquid product. An argument for the latter is supported by the fact that since, in addition to difluoramine, difluoro-urea has been isolated from the fluorinated liquid, other forms such

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as the monofluoro and trifluoro urea may well exist in the liquid, but have not yet been identified. It is reasonable to postulate the reaction of difluorourea going to difluoroamine and isocyanic acid.



A similar reaction when applied to mono- or trifluorourea might yield as yet unobserved products such as  $\text{H}_2\text{NF}$ . While it has not been established quantitatively, there has been indication that the fluorinated liquid which gives the greatest yield of difluoroamine yields the least difluorourea and vice versa. It may well be possible to maximize either yield, or to optimize the yield of both by suitable modifications of conditions and apparatus.

Two exploratory direct fluorinations of cyanoguanidine were made with the view that perhaps cyanodifluoroamine would be one of the products as well as difluoroamine itself. The products were solids with no oxidizing power, and a mixture of gases. This mixture was shown by infrared analysis to be mainly  $\text{CF}_4$ ,  $\text{CF}_3\text{NF}_2$ ,  $\text{HNF}_2$ ,  $\text{FCN}$  (Ref. 5, 6), and smaller amounts of  $(\text{CF}_3)_2\text{NF}$ ,  $(\text{CF}_3)_3\text{N}$ ,  $\text{N}_2\text{F}_2$ ,  $\text{N}_2\text{F}_4$ , and  $\text{SiF}_4$ . There were some unidentified peaks but these were not in the N-F band region. These results agree well with those of Minnesota Mining and Manufacturing Co. (Ref. 7)

#### CHEMISTRY OF DIFLUORAMINE

The acid character of difluoroamine has been previously reported by Rocketdyne and others. The reactions of difluoroamine with potassium fluoride and with trimethylamine have been reported recently (Ref. 1).

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The formation of a weak compound of KF with difluoramine was demonstrated, and we are reporting our results with other metal fluorides as well as other bases.

Difluoramine-Alkali Metal Fluorides\*

The low temperature reaction of KF with  $\text{HNF}_2$  results in the formation of an adduct with a heat of dissociation of 6.7 Kcal/mole. Rubidium fluoride is a stronger base and, as expected, forms a more stable compound. From the plot of the dissociation pressure versus the reciprocal of temperature, the following expression was obtained for the adduct with RbF.

$$\log_{10} K_{p_{\text{mm}}} = \frac{-2166}{T} + 10.338$$

From the slope of the straight line represented by the above equation, the heat of dissociation for the reaction was calculated to be 9.9 Kcal/mole

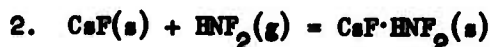
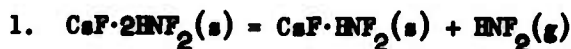


A similar study of difluoramine over CsF was conducted. A complex was formed; however, its behavior was different from the other complexes discussed above. The vapor pressure of the complex was measured as 1.2 mm at -64.8 C. This pressure is higher by 0.8 mm for that of RbF complex at the same temperature. This was surprising since CsF is a stronger base than RbF and it would be expected that difluoramine would be more tightly bound to CsF than to RbF. However, it was found that

\*Work on difluoramine-alkali fluorides was supported in part by the Air Force under Contract AF 33(616)-6768.

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approximately 50 percent of the  $\text{HNF}_2$  introduced over the  $\text{CsF}$  could be pumped off at  $-65^\circ\text{C}$ , after which the pressure exhibited by the solid complex was essentially zero. A tentative explanation for the anomalous behavior involves a complex equilibrium:



The formation of a higher complex such as the 2:1 complex in 1. might account for the higher dissociation pressure initially observed. However, the reaction shown in 2. once equilibrium in 1. has been established, might be slow due to the limited surface area of the  $\text{CsF}$ . After the loosely bound  $\text{HNF}_2$  was pumped off, (Eq. 1,) the remaining complex is tightly bound at  $-65^\circ\text{C}$ .

No dissociation pressures were measured for  $\text{CsF} \cdot \text{HNF}_2$  because of the explosive nature of the complex. In every experiment, a sharp detonation occurred upon warming the complex to about  $0^\circ\text{C}$ .

Fluorides other than those of the alkali metals were used in an attempt to convert  $\text{HNF}_2$  to  $\text{N}_2\text{F}_2$ . No effect was noted when  $\text{HNF}_2$  was contacted with  $\text{CaF}_2$  and  $\text{NiF}_2$  at ambient temperature.

#### Reaction of Difluoramine with Tetramethylammonium Hydroxide

The possible interaction of a strong amine base, trimethylamine with  $\text{HNF}_2$  to form the  $\text{NF}_2^-$  ion was examined. The results were not reproducible. A strong base with a large cation, tetramethylammonium hydroxide, was tried next.

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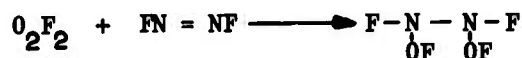
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The tetramethylammonium hydroxide was obtained as a 10 percent aqueous solution, and vacuum evaporation at room temperature yielded white hydrated crystals having from 4 to 5 moles of water of hydration. Warming to 65 C with pumping gave the anhydrous base. Neither the hydrated nor anhydrous base was found to be soluble in dimethyl ether, or tetrahydrofuran; however both were quite soluble in methanol.

Although residues ranging from white solids to yellow liquids were obtained, only a few showed any oxidizing power and these were not reproducible. Three reactions resulted in sharp detonations, each occurring just after condensing the difluoramine into the reactor at -142 C and bringing it up to -80 C. A probable cause of these explosions is that the difluoramine did not vaporize before it ran down the walls of the reactor. The liquid, on contacting the base, reacted exothermically, thereby detonating the difluoramine.

#### O F COMPOUNDS

New compounds containing the OF moiety are of great interest as oxidizers. To this end, the reaction of  $O_2F_2$  with  $N_2F_2$  was investigated in the hope of obtaining a new oxidizer according to the following equation:



To test the possibility of  $O_2F_2$  adding to the double bond of  $N_2F_2$ , the two compounds were mixed in a cold trap. The contact time and temperature were varied from simple warming from -196 C to room temperature to allowing a contact time of 30 minutes at -95 C. Higher temperatures were not used due to the well-known instability of  $O_2F_2$ . No indications were found that any reaction took place between the two compounds.

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Other evidence in the literature points to the reluctance of  $O_2F_2$  in yielding OF radicals. The reaction of  $O_2F_2$  with  $N_2F_4$  (Ref. 8) did not yield any OF species, nor did OF compounds result from the reaction with tetrafluoroethylene and 3-chloroperfluoropropene (Ref. 9). On the other hand,  $N_2F_4$  did not add to the double bond of difluorodiazine (Ref. 10), indicating that the double bond is an unreactive one. It thus seems that the reaction is energetically unfavored, and that some source of energy must be provided to induce the desired path. This will be attempted by having the reactants excited by an electric discharge in a cell cooled to an appropriate temperature, where  $O_2F_2$  and  $N_2F_2$  have a vapor pressure of a few millimeters.

#### ELECTRIC DISCHARGE REACTIONS

Difluorodiazine was exposed to a glow discharge at -156 C to test its stability under these conditions, and also to determine if any condensation product of new binary NF compounds would result. The only products found were unreacted  $N_2F_2$ , noncondensable gas, SiF and nitrogen oxides.

During the course of preparing  $O_2F_2$ , a mixture of gases was employed that contained oxygen, fluorine and some nitrogen. Nitrogen trifluoride was found among the products. It seemed quite possible that the  $NF_3$  had been produced from nitrogen and fluorine in the discharge at -196 C. Previous findings show that at higher temperatures  $NF_3$  decomposes in an electric discharge back to the elements (Ref. 11) with small amounts of  $N_2F_4$  and  $N_2F_2$  also forming. A report also exists on the formation of  $NF_3$  from the electric discharge reaction of  $O_2F$ ,  $N_2$  and  $O_2$  mixtures (Ref. 12). There are, however, several reports in the literature that fluorine and nitrogen do not combine under these

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conditions. The first was by O. Ruff (Ref. 13) and more recent reports in the classified literature had apparently confirmed this. (Ref. 12,14)

In a test experiment, a mixture containing 75 percent fluorine and 25 percent nitrogen was subjected to a glow discharge at -196 C. A 15 percent yield of nitrogen trifluoride was obtained. No effort was made to maximize the yield, so that 15 percent is not necessarily the best obtainable. An unstable species was also formed, and is under investigation. As always,  $\text{SiF}_4$  and nitrogen oxides were formed, resulting from the attack on glass by the mixture during discharge. This is the first time, to our knowledge, that elemental nitrogen and fluorine have been combined.

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**EXPERIMENTAL SECTION**

**ISOLATION AND PURIFICATION OF uns-DIFLUOROUREA**

After difluoramine had been distilled from the fluorinated urea liquid, about 5 ml of the liquid residue were placed in a polyethylene bottle and extracted three times with 20 ml portions of dichloromethane. The dichloromethane solutions were decanted from the residue, combined, and placed in a wide mouth polyethylene evaporating dish. The solution was then evaporated to dryness under gradually reduced pressure in a vacuum desiccator. The conventional desiccator cover used during evaporation was replaced with a four-hole desiccator cover, housing the sublimation apparatus. To provide a cold surface for the sublimation, a round bottom flask coated with polyethylene was mounted in the center hole of the cover. The flask completely covered the mouth of the evaporating dish and was attached to it securely. Ice water was circulated through the flask. The bottom of the sample dish was warmed by a spiral of copper tubing through which water at about 50 C was circulated. The warm water connections were passed through an air tight seal in the desiccator cover. The two remaining holes in the cover were fitted with stopcocks for circulating dry nitrogen through the desiccator. After about two hours of operation, the apparatus was disassembled in a dry box and the sublimed material transferred to a polyethylene vial for storage. Occasional difficulties were observed in the sublimation due to the presence of water.

Other samples were obtained from the -80 C trap where rings of comparatively pure compound were formed on the warm arm of the trap. These samples were also purified by sublimation.



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#### Analysis of Difluorourea

The Kjeldahl analyses were conducted in two ways. Adding the difluorourea directly to concentrated sulfuric acid resulted in quantitative release of the  $\text{NF}_2$  group presumably as difluoramine. Subsequent analyses gave the amino nitrogen quantitatively. Prior addition of hydriodic acid before treatment with concentrated sulfuric acid yielded the total nitrogen.

The analytical methods for active and hydrolyzable fluorine have already been described. (Ref. 15).

#### Fluorination of Urea

Fluorinations 38 through 42 were carried out during this quarter and are summarized in Table 3. Runs No. 39 and 42 both ran smoothly to completion with all the urea being reacted. Run No. 38 was aborted early due to outside interference, and approximately 15 gm of unreacted urea was recovered from the reactor, which had no appreciable oxidizing power. Run No. 40 burned out due to a corroded needle valve in the fluorine line which allowed too great a  $\text{F}_2:\text{N}_2$  ratio. Run No. 41 proceeded smoothly except that some of the urea sifted through the porous plate to the bottom of the reactor and did not become fluorinated. In Run No. 40 a  $-156^\circ\text{C}$  cold trap was placed down stream of the reactor and analysis of the gas condensed in this trap during the fluorination showed  $\text{CO}_2$  and  $\text{SiF}_4$  as the main products with smaller amounts of  $\text{CF}_4$  and  $\text{COF}_2$ .

The distillations of the fluorinated urea liquids (Table 3) to prepare difluoramine were carried out at room temperature and at a pressure of less than 2mm of Hg. Distillation times shown are total times on each aliquot. The age of the liquid is determined from the date of fluorination to the date of distillation. In all cases, large quantities of  $\text{CO}_2$  and  $\text{SiF}_4$  were obtained.

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**FLUORINATION DATA**

Run No.	Urea, g <sup>m</sup>	Liquid g <sup>m</sup>	Act F %	Tot F %	F <sub>2</sub> g <sup>m</sup>	F <sub>2</sub> -N <sub>2</sub>	F mol
35	60	68.7	12.2	27	36.1	1:4	0.1
36	30	41.4	14.7	43.1	26.6	1:4.7	0.1
37	90	136.1	18.6		NOT KNOWN		
38	30	19.8	16.6	38.1	20.5	1:7	0.1
39*	90	141	17.3	43.4	110.6	1:4	0.5
40	Burned out due to corroded valve						
41	90	70	7.0%		35.9	1:4	0.27
42	60	80.6	12%		38	1:3.5	0.25

\* Fluorinated Ureas Liquid No. 39 was divided into two parts and is designated 39-1 and 39-2

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**TABLE 3**

**PREPARATIONS OF DIFLUORAMINE**

**DISTILLATION DATA**

$F_2-N_2$	$F_2$ mole/hr	Dist. Aliquot	Liquid gm	Dist. Time, hr	Liq. Age Days	$HNH_2$ cc	$HNH_2$ % on $F_2$	$HNH_2$ % on Act F
1:4	0.19	C	9.8	3.0	218	28	1.8	4.0
1:4.7	0.14	B	5.3	3.0	98	170	12.6	37.1
		C	5.3	4.0	100	197	14.6	42.9
		D	10.1	4.0	104	370	14.4	42.2
		E	9.1	4.0	107	285	12.3	36.2
		F	11.2	4.0	118	323	11.3	33.3
KNOWN		J	15.0	4.0	64	140		8.5
		K	16.6	3.0	65	160		8.8
1:7	0.16	A	16.7	4.0	47	34	0.9	2.1
1:4	0.52	39-2-A	6.1	4.0	10	52	3.3	8.3
		B	12.0	4.0	38	113	3.7	9.2
		C	11.7	3.0	43	107	3.6	9.0
		D	10.7	4.0	44	92	3.4	8.4
		E	10.4	4.0	45	85	3.2	8.0
		39-1-A	9.5	3.0	64	93	3.8	9.6
		B	10.3	3.0	67	82	3.1	7.8
1:4	0.27							
1:3.5	0.25							

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**FLUORINATION OF OTHER SOLID NITROGEN COMPOUNDS**

These fluorinations were run in the same reactor and utilized the same conditions as with urea.

**Fluorination of Cyanoguanidine**

**Test No. 1**

Cyanoguanidine	=	8.4 g. (.1 mole)
Fluorine	=	3.8 g. (.1 mole)
Fluorine flowrate	=	0.1 mole/hr
Fluorination time	=	1 hr
Fluorine:Nitrogen ratio	=	1:10

A -156 C trap was used downstream of the reactor to capture gaseous products passing through the reactor. The cyanoguanidine did not yield a liquid when fluorinated but rather a small amount of red solid which displayed no oxidizing power. The gaseous products from the trap were examined by infrared analyses and found to contain  $\text{CF}_4$ ,  $\text{BNF}_2$ ,  $\text{CF}_3\text{NF}_2$  and small amounts of  $\text{SiF}_4$ ,  $\text{N}_2\text{F}_2$ ,  $\text{N}_2\text{F}_4$  and  $\text{NF}_3$ .

**Fluorination of Cyanoguanidine**

**Test No. 2**

Cyanoguanidine	=	42 g. (.5 moles)
Fluorine	=	19 g. (.5 moles)
Fluorine flowrate	=	0.1 mole/hr
Fluorination time	=	5 hrs
Fluorine:Nitrogen ratio	=	1:8

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In this run, most of the cyanoguanidine was found as a large brick-red clinker in the reactor but no liquid was formed. The gaseous products were again trapped at  $-152^{\circ}\text{C}$  and examined by infrared analyses. The gaseous products identified were  $\text{FCN}$ ,  $\text{HNF}_2$ ,  $\text{CF}_3\text{NF}_2$ ,  $(\text{CF}_3)_2\text{NF}$ ,  $(\text{CF}_3)_2\text{NH}$  and  $\text{SiF}_4$ . There were a few unidentified bands but these were not in the N-F region.

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Dissociation Pressure of Difluoramine Over Rubidium Fluoride

The system and techniques used to perform the measurements on the RbF-HNF<sub>2</sub> system were the same as described in the previous report. The results of the measurements are given in Table 4. Higher temperatures were not used to prevent the formation of difluorodiazine.

TABLE 4

VAPOR PRESSURE OF HNF<sub>2</sub> OVER RbF

Temp., C	Pressure (obs.) mm	Pressure (calc.) mm
-81.6	0.0	--
-72.0	0.0	--
-65.0	0.8	0.86
-57.8	1.9	1.9
-45.8	6.5	6.5
-31.6	23.5	23.6

Difluoramine and Tetramethylammonium Hydroxide

The general procedure in reacting difluoramine with tetramethylammonium hydroxide follows. The solid base was dissolved in the solvent and then the difluoramine was condensed in the reactor at -142 C. Most runs were allowed to equilibrate at -80 C for one hour before vacuum distillation.

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The usual gaseous products of distillation were difluoramine and traces of the solvent. The residues ranged from white or yellow solids to yellow liquids with little oxidizing power except for Run No. 6. This run was not evaporated before testing for active fluorine. Even so, all the active fluorine was not accounted for; only 70 percent of theory was found by HI addition to the solution at -80 C.

Table 5 shows the amount of difluoramine recovered by distillation and the percent accounted for in both the gaseous and solid products. Little non-condensable gas was found in most cases and in Run No. 18 may have been due to a leak. In Run No. 12, the noncondensable gas may have come from the products of combustion as a flash took place in the reactor on warming from -80 C to room temperature. Runs No. 14, 15 and 16 all exploded on changing baths on the reactors from -142 to -80 C.

Dioxygen Difluoride ( $O_2F_2$ ) and Difluorodiazine

The apparatus and procedure for the synthesis of  $O_2F_2$  was described in the last report (Ref. 1).

The procedure generally consisted in transferring an excess of  $O_2F_2$  from the reactor onto a trap cooled at -196 C, and condensing  $N_2F_2$  into the same trap. The temperature of the trap and contact time was varied from experiment to experiment. The trap was designed so that it was almost completely immersed in the slush bath, in order to minimize decomposition of the  $O_2F_2$  vapor. This proved successful, and  $O_2F_2$  could be kept this way for over 30 min at -95 C.



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TABLE 1

REACTION OF  $\text{HNf}_2$  A

Run No.	$(\text{CH}_3)_4\text{NOH}$ g	Form	Solvent	Amount	$\text{HNf}_2$ in cc $25^\circ\text{C}$	$\text{HNf}_2$ out, cc $25^\circ\text{C}$	Perc Acco
1	.1975	hyd	$(\text{CH}_3)_2\text{O}$	86.4 cc	14.5	mix $\text{HNf}_2$ , $(\text{CH}_3)_2\text{O}$	
2	.240	hyd	$(\text{CH}_3)_2\text{O}$ (mixture from #1)			mix $\text{HNf}_2$ , $(\text{CH}_3)_2\text{O}$	
3	.1250	hyd	aqueous		10.1	9.3	
4	.0233	hyd	$\text{CH}_3\text{OH}$	1 ml	10.8	mix $\text{HNf}_2$ , $\text{CH}_3\text{OH}$	
5	.125	hyd	aqueous		21.6	23.6 $\text{HNf}_2$ trace $\text{CH}_3\text{OH}$	
6	.0190	anhyd	$\text{CH}_3\text{OH}$	1 ml	10.6	none	7
7	.0056	anhyd	$\text{CH}_3\text{OH}$	1 ml	10.2	trace	
8	.0676	hyd	none		8.6	4.8	2
9	.1262	hyd	none		26.4	12.1	
10	.2785	hyd	none		25.1	8.8	
11	.1768	hyd	none		20.8	?	3
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TABLE 5

REACTION OF  $\text{HNf}_2$  AND  $(\text{CH}_3)_4\text{NOH}$

in STP	$\text{HNf}_2$ out, cc STP	Percent $\text{NF}_2$ Accounted for	N.C.G. cc STP	Remarks
5	mix $\text{HNf}_2$ , $(\text{CH}_3)_2\text{O}$	0	none	$(\text{CH}_3)_4\text{NOH}$ insoluble in $(\text{CH}_3)_2\text{O}$ , turned yellow
	mix $\text{HNf}_2$ , $(\text{CH}_3)_2\text{O}$	0	2.5	The same as in Run No. 1
	9.3	0	trace	Crystals form when liquid evap. under vacuum
3	mix $\text{HNf}_2$ , $\text{CH}_3\text{OH}$	0	none	Residue left on evap. under vacuum
6	23.6 $\text{HNf}_2$ trace $\text{CH}_3\text{OH}$	0	none	Vacuum evap. produced residue
6	none	70	30	Not evap., solution tested
2	trace	0	2	Evap. under vacuum left white film
6	4.8	27	1	A liquid formed on warming to room temperature
4	12.1	0	a few	Yellow liquid at room temperature
2	8.8	0	4	Warmed to 50 C, the liquid went to paste
3	?	3.4	15.7	On warming there was a flash in the reactor
				Contaminated with $(\text{CH}_3)_2\text{O}$ , not run

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Run No.	$(\text{CH}_3)_4\text{NOH}$ gm	Form	Solvent	Amount	$\text{HNF}_2$ in cc STP	$\text{HNF}_2$ out, cc STP
13	.0657	hyd	none		26.2	14.8
14	.2982	hyd	none		37.8	
15	1.1169	anhyd	none		23.0	
16	.4319	anhyd	THF	2 ml	28.0	
17						
18	.1410	anhyd	$\text{CH}_3\text{OH}$	3 ml	30.5 in 1 ml $\text{CH}_3\text{OH}$	none
19	.2678	anhyd	$\text{CH}_3\text{OH}$	3 ml	31.9 in 1 ml $\text{CH}_3\text{OH}$	none

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**TABLE 5**  
**(Continued)**

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$\text{NF}_2$ in cc STP	$\text{NF}_2$ out, cc STP	Percent $\text{NF}_2$ Accounted for	N.C.G. cc STP	Remarks
6.2	14.8	0		The same liquid as No. 8
7.8				Explosion occurred during warming from -142 C to -80 C
3.0				Same
3.0				Same except that the solid was not soluble, turned yellow
				Not run, damaged by explosion of No. 16
0.5 in 1 $\text{CH}_3\text{OH}$	none	11	30	Most of the $\text{CH}_3\text{OH}$ removed before titration
1.9 in 1 $\text{CH}_3\text{OH}$	none	16	a few	A white solid observed at -80 C but absent at room temperature, probably $\text{CO}_2$

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Reactions were tried where the two compounds were warmed from -196 C to room temperature, reacted at -95 C for 5 min and 30 min, and at -142 C for 15 min. In the latter case, the  $N_2F_2$  was quantitatively recovered. Among the products were found unreacted  $N_2F_2$ , noncondensibles from the decomposition of  $O_2F_2$ , and  $SiF_4$ . Some unidentified fluorocarbons, as well as  $CF_4$  and  $COF_2$  were frequently encountered, due to the action of fluorine on the stopcock grease.

#### Difluorodiazine Under Electric Discharge

Difluorodiazine (12.5cc) was admitted into the glow discharge cell at -156 C. The vapor pressure of  $N_2F_2$  at this temperature is 8 mm. The pressure in the system quickly rose, once the discharge was initiated. The experiment was interrupted, once the pressure had increased to a point where a discharge could no longer be maintained, and 9.1 cc of impure  $N_2F_2$  was recovered from the noncondensable gases formed. Infra-red examination showed the impurities to be  $N_2O$ ,  $COF_2$ ,  $SiF_4$  and fluorocarbons.

#### Synthesis of Nitrogen Trifluoride

A mixture of nitrogen (10.5 cc) and fluorine (34 cc) was submitted to an electric discharge (10-15 ma), 5000 volts, at -196 C. The pressure in the reactor was maintained between 10 to 17 mm by adding gas to the system as it was consumed. After 29 cc of the mixture had been reacted, the discharge cell was allowed to warm up with pumping, the gases passing through a -196 C and -210 C (solid nitrogen) trap.

The -210 C trap afforded  $NF_3$  (3.2 cc), contaminated with a trace of  $CF_4$ . The -196 C trap contained 4.9 cc of gas which, however, could not be completely recondensed. After pumping off the noncondensibles, 2.6 cc remained, which were mainly  $SiF_4$ ,  $COF_2$ ,  $N_2O$ , and some C-F compound.

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Further work is contemplated to identify the unstable species, and to determine the best conditions for the formation of  $\text{NF}_3$ .

Essentially the same experiment was done with a 50 percent fluorine-nitrogen mixture, except that a  $-210^\circ\text{C}$  trap was not employed. No evidence was found for the presence of  $\text{N}_2\text{F}_2$  or  $\text{N}_2\text{F}_4$ .

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**CONCLUSIONS AND FUTURE WORK**

The isolation of uns-difluorourea from the fluorination products of urea has provided a new NF intermediate for further research as well as suggested methods for preparing other solid oxidizing species. As a result, work on the fluorination of nitrogen compounds other than urea has been intensified.

The formation of adducts of difluoramine with metallic fluorides is of intrinsic interest in the theory of acids and bases. The reactions of bound difluoramine with other materials may provide additional synthetic routes to NF compounds. The possibility of ionic reactions are not excluded.

The preparation of  $\text{NF}_3$  by direct combination of the elements by electrical excitation suggests that an alternate process for the preparation of this key intermediate may be practical. Work on electrical discharge reactions will be continued.

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